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Preparation of hydrophobic silica aerogel with kaolin dried at ambient pressure

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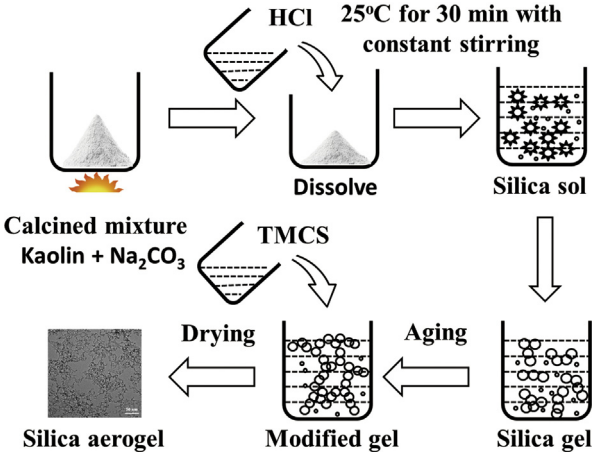
HIGHLIGHTS

- A new method for preparing hydrophobic silica aerogel with kaolin as raw material is proposed.
- The method uses the abundant clay kaolin as raw material.
- The method lowers the cost of silica aerogel compared to using organosilane as raw material.
- The concentration of HCl solution affects greatly the pore structure of aerogel with an optimal value of 4 mol/L.
- Hydrophobic modification of aerogel optimizes its pore structure.

GRAPHICAL ABSTRACT



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ABSTRACT

A method for preparing hydrophobic silica aerogel with kaolin as raw material and dried at ambient pressure is proposed. The process of preparing the aerogel consists of three stages including activation of kaolin, preparation of wet silica gel and hydrophobic modification. The effects of hydrochloric acid concentration on the physical properties and structures of the silica aerogel are investigated. Effects of removing Na^+ from the solvent solution on the structure and properties of aerogel are discussed. The aerogel obtained with kaolin has comparable structure and property to those prepared with other more expensive silica sources. The newly proposed method is expected to simplify the manufacturing technique, to shorten the production time and to reduce the costs of silica aerogel.

1. Introduction

Aerogel are sol–gel material dried in a strictly controlled process to avoid pore collapse, leaving an intact solid nanostructure in a material that contains 90–99% of air by volume [1]. Silica

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aerogel has generally an open structure with a very low density (typically 0.03 g/cm^3), high specific surface area (600–1000 m^2/g), extremely high porosity (90%–99%) and low thermal conductivity (0.02 W/mK) [2–4]. The unique combination of thermal and structural properties makes it an attractive material for a variety of applications ranging from platforms for chemical sensors to thermal insulation [5–7]. However, silica aerogel contains normally polar OH groups on its surface that will potentially generate hydrogen bonding with H_2O [8]. If exposed to ambient air, particularly in a humid environment, the aerogel deteriorates remarkably over time [9,10]. The structural instability of silica aerogel limits its applications, which demands further research. Hydrophobic modification of silica aerogel with large number of non-polar side groups (Si–R, where R is Vinyl, Alkyl, or Aryl groups) on the surface to obtain a surface structure that is water-repelling has been developed [11,12]. It has been proven to promote the stability of the aerogel in regard to applications in a humid environment. Hydrophobic aerogels can also be used as self-cleaning coatings in buildings and constructions. Feasibilities of using hydrophobic aerogels for oil spill clean-up and for surface protection of structure from corrosion of the environment have been proved [13,14].

Three major techniques have been proposed for preparing hydrophobic silica aerogel, i.e. vapor deposition [15], sol-gel techniques and derivatization method, of which the sol-gel technique is most widely used [16–18]. The sol–gel process is based on polymerization of silicon-containing precursors to form a sol and then a wet gel in which the pores are filled with solvent containing by-product of the reaction. In order to obtain an aerogel from the wet gel, extracting the solvent without causing pore collapse is necessary, leaving the silica nanostructure intact and dry. The most well developed method is to use the tetramethoxysilane (TMOS, $Si(OCH_3)_4$), tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) to replace the solvent material followed by supercritical drying [12,19]. The supercritical drying method avoids capillary stresses and the associated drying shrinkage by removing the solvent from the sol–gel matrix as a supercritical fluid [20]. The supercritical condition involves normally high temperature (300 °C) and pressure (63 bar) [4]. The silica aerogel obtained has high purity, good stability and high performances. However, its production costs are also relatively high due to the expensive organic alkoxides (TMOS, TEOS) and the supercritical drying condition used in the technique.

Preparation of silica aerogels with low cost materials and drying condition has attracted great attention in the past years [21–23]. Industrial by-products rich in silica such as fly ash, rice husk ash and used bagasse ashes are proven to have great potential as raw material for preparing silica aerogels [24–26]. However, their technical properties such as composition and reactivity vary in a broad range since they are by-products from other industries, causing large variations in the quality of the aerogel products.

Kaolin is an abundant clay and its main oxide compositions are SiO_2 and Al_2O_3. Its main mineral composition is kaolinite, widely used in papermaking and ceramic industry [27,28]. Kaolin has been proven to be a suitable raw material for preparing amorphous silica gel [29]. The kaolin can be thermally activated, producing reactive meta-kaolin. The high silica content of kaolin and high reactivity of the meta-kaolin make it an ideal raw material for preparing silica aerogel, which is rarely reported previously.

In this study, a method of preparing hydrophobic silica aerogel with kaolin as raw material and dried at ambient pressure is proposed. The newly proposed method uses the highly abundant kaolin clay as the raw material instead of the more expensive synthetic silicate sources. It is expected to lower the production cost of silica aerogel and shorten the production time compared to the use of other silica sources.

Table 1
Oxide compositions of kaolin clay used in the experiment.

Oxide	SiO_2	Al_2O_3	Na_2O	K_2O	CaO	Fe_2O_3	LOI[a]
Mass fraction (%)	49.83	33.60	0.48	0.50	0.07	0.65	13.55

[a] Loss on ignition at 1000 °C.

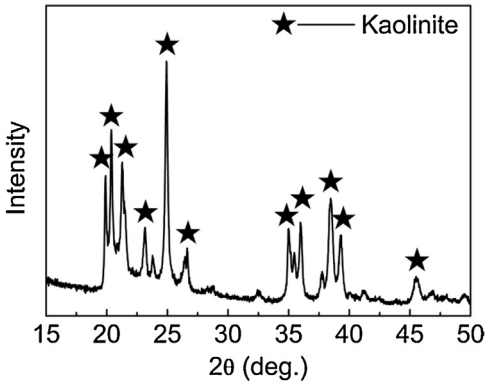

Fig. 1. XRD patterns of the kaolin clay.

2. Material and methods

Kaolin clay from Maoming, China, is firstly dried at 60 °C, ground to pass the 150 μm sieve and the obtained powder is then analyzed. The oxide compositions and volatile contents are listed in Table 1. The kaolin clay contains about 50% silica (by mass and henceforth), followed by about 34% alumina. The X-ray diffraction (XRD) pattern of kaolin is shown in Fig. 1 (obtained with Bruker D8 Advance, Target Cu, Kα = 1.5406 Å, step size 0.019°, measuring speed 141.8 s/step, start position 5° and end position 80°). The main mineral phase in the clay is kaolinite. The scanning electron microscopy (SEM) images (obtained with JSM-5610LV, accelerating voltage 20 kV) are shown in Fig. 2. The particle shape of kaolin clay is generally round with a smooth surface.

Sodium carbonate (Na_2CO_3, Sinopharm, AR grade), hydrochloric solutions (AR grade), ammonium hydroxide solution (NH_4OH, Sinopharm, pH = 12), ethyl alcohol (AR grade), *n*-hexane (AR grade), trimethylchlorosilane (TMCS, AR grade), Na-type 732 polystyrene cation exchange resin and de-ionized water are used during the synthesis and treatment processes of the silica aerogel.

The density of the aerogel is measured following the method of Zhu et al. [30]. A glass cylinder with a volume of 5 mL is firstly weighed as m_1, and then filled with silica aerogel powder, weighed as m_2. After jolting the cylinder filled with aerogel for 500 times, the volume of the compacted aerogel is read (V). The density of silica aerogel is calculated as:

$$\rho = (m_2 - m_1)/V \quad (1)$$

The experiment is repeated for three times for each sample and the density is the average value from the three measurements.

Fourier transform infrared (FTIR) spectra of silica aerogel are recorded with a Fourier transform infrared spectroscopy (Model Thermo Nicolet Nexus) in the range 4000–400 cm^{-1} with a 4 cm^{-1} resolution by measuring the IR absorbance of KBr disk containing the samples. The specific surface area, pore volume and pore sizes of the aerogel are measured using a nitrogen gas adsorption-desorption method (ASAP 2020 M, Micromeritics Instrument Corp) following the method reported in literatures [31,32]. The silica aerogel sample is dried at 90 °C for 2 h, and the adsorption–desorption isotherms are obtained at −196.15 °C. The specific surface area is calculated by using the Brunauer–Emmett–Teller (BET) method at $P/P_0 < 0.3$. Transmis-